Decomposition of nonafluoropentanoic acid by heteropolyacid photocatalyst $H_3PW_{12}O_{40}$ in aqueous solution

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Abstract

Nonafluoropentanoic acid (C_4F_9COOH; NFPA), which is a typical perfluorinated acid, was decomposed to F^- and CO_2 with a water-soluble tungstic heteropolyacid photocatalyst, $H_3PW_{12}O_{40}$. The catalytic reaction proceeded in water at room temperature under UV-Vis irradiation in the presence of oxygen. The reaction system produced no trace of environmentally undesirable species, such as CF_4 and CF_3H. In addition to F^- ions, a small amount of a one-CF_2-unit-shortened species, heptafluorobutyric acid (C_3F_7COOH; HFBA), was formed. The reaction mechanism involves precomplexation between $[PW_{12}O_{40}]^{3-}$ and NFPA and subsequent redox reactions.
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1. Introduction

Fluorinated organic compounds are widely used in industrial applications [1]. For example, perfluorinated acids (mainly carboxylic and sulfonic acids) and their derivatives are widely used as surfactants, such as emulsifying agents in polymer synthesis, surface treatment agents in photolithography, fire retardants, carpet cleaners, paper coatings, and so on [1–3]. As the use of perfluorinated acids has increased, some of them have recently been detected in environmental waters and in animals [4–7], and analytical studies have revealed their bioaccumulative and biomagnificative properties. Perfluorinated carboxylic acids are also emitted by thermal decomposition of commercial fluoropolymers [8]. Fluorochemical manufacturing sites are significant stationary sources [4,9] The strong C–F bonds of perfluorinated acids make them quite stable, and they have no known natural decomposition processes [2,3]. Hence, to suppress the accumulation of these compounds in the environment, an artificial decomposition method of converting them to environmentally harmless species under mild

conditions is desirable as a measure against emission from stationary sources. The method should involve cleavage of the C–F bonds of perfluoroalkyl (CF_3-, $-CF_2-$) groups to form F^- ions, which can easily combine with Ca^{2+} to form environmentally harmless CaF_2. However, because the C–F bond is the strongest bond among the bonds involving carbon, it is difficult to cleave. Although the heterogeneous photocatalyst TiO_2 has been widely used for the decomposition of water pollutants [10], the reactivity of TiO_2 toward trifluoroacetic acid (CF_3COOH; TFA), the simplest perfluorinated carboxylic acid, is estimated to be very low [11].

Water-soluble heteropolyacids are attractive candidates for photocatalysts for the decomposition of perfluorinated acids in water because of their multielectron-capabilities and their stability under highly acidic conditions [12–14]. Furthermore, the catalysts are recyclable through selective recovery from reaction solutions by ether treatment [15].

Herein, we describe the effective decomposition of nonafluoropentanoic acid (C_4F_9COOH; NFPA), which is a typical perfluorinated carboxylic acid being used as an industrial surfactant, in a homogeneous catalytic system consisting of the heteropolyacid photocatalyst $H_3PW_{12}O_{40}\cdot 6H_2O$ (**1**), water, and oxygen.

2. Experimental

2.1. Materials

Heteropolyacid **1** was obtained from Wako Pure Chemical Industries Ltd. and purified by ether extraction and recrystallization from water. NFPA, heptafluorobutyric acid (C_3F_7COOH; HFBA), pentafluoropropionic acid (C_2F_5COOH; PFPA), and TFA were purchased from Tokyo Kasei Kogyo Co., Ltd. Other reagents were of high purity and were obtained from Kanto Chemical Co., Inc., and Wako Pure Chemical Industries Ltd.

2.2. Photochemical procedures

The photochemical reactions were carried out in a cylindrical pressure-resistant Inconel reactor ($200\,cm^3$, $4.5\,cm$ i.d.) equipped with a sapphire window on the top for the introduction of light. The inner wall of the reactor was coated with poly(tetrafluoroethylene). A small gold vessel ($25\,cm^3$, $3.8\,cm$ i.d.), which was stable to highly acidic solutions, was placed in the reactor and filled with $23\,cm^3$ of an aqueous solution containing **1** ($0.46\,g$, 1.54×10^{-4} mol; $6.70\,mM$) and a 5–50-fold molar excess of NFPA. The pH of the solution was ∼0.8. The reactor was purged and then pressurized to $0.55\,MPa$ with oxygen gas, because pressurized oxygen enhanced the photocatalytic oxidation ability of **1** [15,16].

Next, the solution was irradiated with UV-Vis light from a $500\,W$ high-pressure mercury lamp (Ushio USH-500SC). For the irradiation, a water filter and a liquid-type optical fiber (Ushio LF8L1000) were used. During irradiation, the temperature of the solution was maintained at $25\,°C$ by using a water bath. After irradiation, the pressure was released, and the gas was collected in a sampling bag and subjected to GC and GCMS. The liquid phase was subjected to ion chromatography and ion-exclusion chromatography. For the photoreactions under argon, normal-pressure ($0.10\,MPa$) argon was used instead of oxygen.

To examine the catalyst degradation, $0.10\,cm^3$ of the reaction solution after $96\,h$ of irradiation was diluted with MeCN up to $50\,cm^3$, and then subjected to UV-Vis spectral measurements. The absorbance at $265.5\,nm$ (absorption maximum of the ligand-to-metal charge-transfer band of **1**) was compared with that taken before irradiation. In addition, a few drops of the reaction mixture were evaporated to dryness and then subjected to IR (KBr) measurements.

The photochemical reactions with irradiation of $313\,nm$ monochromatic light were also carried out using a band pass filter. For the monochromatic light experiments, a $K_3Fe_2(C_2O_4)_3$ actinometer was used to measure the incident light intensity. The apparent quantum yield for the decomposition of NFPA was determined by [NFPA decomposition rate ($mol\,h^{-1}$)]/[light intensity (einstein h^{-1}); 1 einstein = 6.022×10^{23} photons].

2.3. Analytical procedures

The GC system consisted of a GL Science GC323 chromatograph with an active carbon column and a thermal conductivity detector. The GCMS system consisted of an HP 5890 gas chromatograph with a column (Chrompack, Poraplot Q, $0.32\,mm$ i.d., $25\,m$) and an HP G1034CJ workstation. The carrier gas was He. Standard samples of CF_3H, CF_4, C_2F_6 and CO_2 were used for quantitative and qualitative analysis. Tosoh 8020 and IC-2001 ion chromatographs were used to measure the amount of F^- ions. The ion-exclusion chromatography system for the analysis of perfluorinated acids consisted of a column (TSKgel Oapak-A, $7.8\,mm$ i.d., $30\,cm$), a pump, and a conductivity detector. The mobile phase was phthalic acid ($2\,mM$) or a mixture (95:5 (v/v)) of phthalic acid ($2\,mM$) and methanol.

3. Results and discussion

3.1. Photocatalysis

Fig. 1 shows the wavelength distributions for the absorption of NFPA and catalyst **1** and the emission from the mercury lamp. Under our reaction conditions, the mercury lamp with filters emitted 260–600 nm light (Fig. 1C). Catalyst **1** absorbed the light from the UV region to 390 nm (Fig. 1B), whereas NFPA had little absorption above 260 nm (Fig. 1A). Hence, **1** was virtually the only species that absorbed the light from the lamp.

Fig. 2 shows the irradiation-time dependence of the photoreaction in which we used a 10-fold molar excess of NFPA relative to **1**. As expected, the amount of NFPA decreased
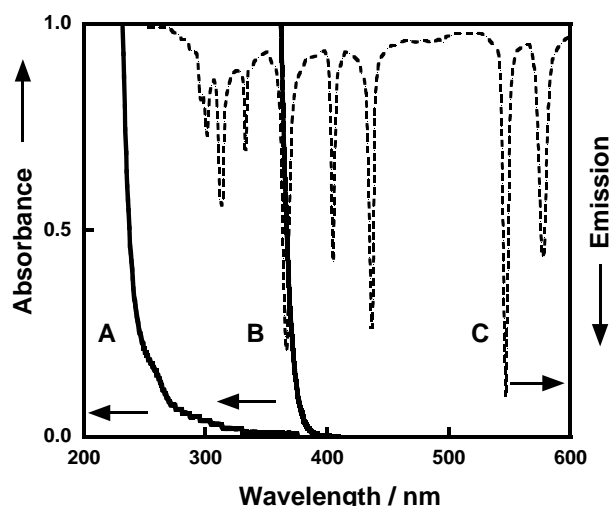

Fig. 1. Wavelength distribution for (A) the absorption of NFPA ($67.4\,mM$ in water), (B) the absorption of catalyst **1** ($6.70\,mM$ in water), and (C) the emission from the mercury lamp. The concentrations of NFPA and **1** were the same as those in the following catalysis experiment (Fig. 2). The path length for the absorption spectral measurements was $1.0\,cm$.
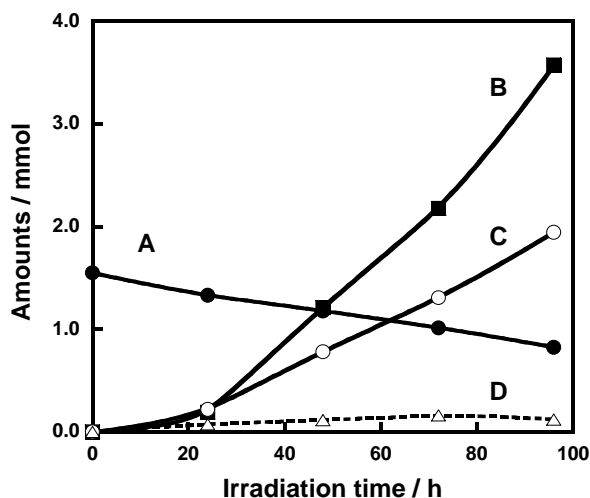
Fig. 2. Irradiation-time dependence of NFPA decomposition: detected molar amounts of (A) NFPA, (B) F^-, (C) CO_2, and (D) HFBA. An aqueous solution ($23\,cm^3$) containing **1** (1.54×10^{-4} mol; 6.70 mM) and NFPA (1.55 mmol; 67.4 mM) was irradiated with a high-pressure mercury lamp under oxygen (0.55 MPa).

with irradiation, and F^- and CO_2 were found as products in the liquid and gas phases, respectively. After 96 h of irradiation, 46.7% of the initial NFPA had been decomposed, which corresponds to a turnover number [(mol of decomposed NFPA)/(mol of initial **1**)] of 4.70. The yields of F^- [(mol of formed F^-; 3.58 mmol)/(mol of initial NFPA $\times$ 9)] and CO_2 [(mol of formed CO_2; 1.94 mmol)/(mol of initial NFPA $\times$ 5)] were 25.7 and 25.0%, respectively. The F^-/CO_2 ratio was almost the same as the F/C ratio of NFPA (9/5). GCMS analysis of the gas phase indicated that the system produced no environmentally undesirable species, such as CF_4 and CF_3H, stable species that have high global warming potentials, at least 3900 and 9400 times as high as CO_2, respectively [17]. CF_4 is often observed in the decomposition of perfluorinated compounds by extremely high energy techniques, such as electron-beam irradiation [18]. Ion-exclusion chromatography revealed the presence of small amounts of the one-CF_2-unit-shortened species, HFBA, in the liquid phase. Ion-chromatography and ion-exclusion chromatography showed no products other than F^- and HFBA in the liquid phase.

The UV-Vis absorption spectrum of the reaction solution after 96 h of irradiation indicated that 95% of initial **1** re-

mained, and the IR spectrum after the reaction showed no sign of the catalyst degradation. Hence, **1** is stable over long periods of irradiation.

While the amounts of F^- and CO_2 increased with increasing irradiation time, the amount of HFBA gradually increased up to 72 h, and then decreased (Fig. 2). If NFPA had simply decomposed to HFBA and F^-, that is, if the F^- ions were derived from only one CF_2 unit of NFPA, the amount of F^- should have been twice the amount of produced HFBA. The much larger amount of F^- produced than that expected indicates either that HFBA was further decomposed or that NFPA produced F^- ions not only through HFBA formation but also through some other decomposition pathway.

In the absence of light irradiation, no reaction occurred (Table 1, entry 2). When the reaction was carried out in the absence of either catalyst **1** or oxygen, little reaction was observed (entries 3 and 4). The combination of **1**, oxygen, and light irradiation is required for effective NFPA decomposition (entry 1). These results clearly indicate that **1** acted as a photocatalyst.

The photocatalytic decomposition of NFPA was greatly affected by the initial amount of NFPA. For a constant amount of **1** and a reaction time of 48 h, the amounts of F^-, CO_2, and HFBA formed and NFPA decomposed all markedly increased as the initial NFPA amount was raised to 3.10 mmol [(initial NFPA)/(initial **1**) molar ratio = 20/1] (Fig. 3). Increasing the initial NFPA amount up to 7.76 mmol [(initial NFPA)/(initial **1**) molar ratio = 50/1] showed the saturation tendency of the reaction, the turnover number reaching 8.02. The reaction's dependence on the initial amount of NFPA can be interpreted on the basis of the precomplexation of **1** and NFPA before the irradiation, as described in the next section.

The decomposition of NFPA using **1** and oxygen was also observed when the monochromatic light (313 nm) was irradiated. When the light intensity was 2.25×10^{-4} einstein h^{-1} and the initial NFPA amount was a 50-fold molar excess relative to **1**, the apparent quantum yield for NFPA decomposition was 0.051.

3.2. Proposed reaction mechanism

3.2.1. Photo-induced redox reaction between *1* and NFPA

The anion part of **1**, $[PW_{12}O_{40}]^{3-}$, is stable below pH 2, and at higher pH, it is partially converted to $[PW_{11}O_{39}]^{7-}$

Table 1
Dependence of the product distribution on catalyst, light irradiation, and reaction atmosphere[a]

Entry	Catalyst	Light	Atmosphere (pressure/MPa)	NFPA decomposed (10^{-4} mol)	F^- formed (10^{-4} mol)	CO_2 formed (10^{-4} mol)	HFBA formed (10^{-4} mol)
1	Present[b]	Present	O_2 (0.55)	3.72	12.1	7.81	1.18
2	Present[b]	None	O_2 (0.55)	ND	ND	ND	ND
3	None	Present	O_2 (0.55)	0.39	ND	0.66	ND
4	Present[b]	Present	Ar (0.10)	0.13	0.49	0.45	ND

[a] Reaction time, 48 h; initial amount of NFPA, 1.55 mmol; reaction solution volume, $23\,cm^3$.
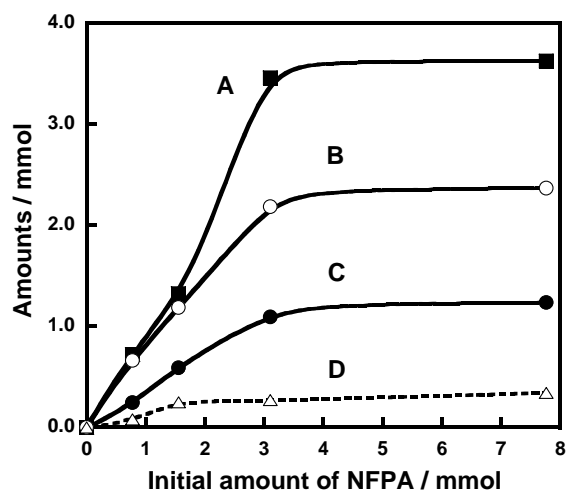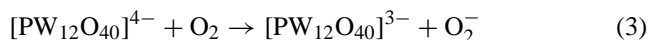[b] Initial amount of **1**, 1.54×10^{-4} mol.

Fig. 3. Dependence of (A) F^- formation, (B) CO_2 formation, (C) NFPA decomposition, and (D) HFBA formation on the initial amount of NFPA. An aqueous solution ($23\,cm^3$) containing **1** (1.54×10^{-4} mol) and NFPA (0.78–7.76 mmol) was irradiated for 48 h under oxygen (0.55 MPa). Although the data for this figure were obtained using irradiation with the same light intensity, the data for 1.55 mmol of initial NFPA in this figure differ somewhat from the data at 48 h in Fig. 2, owing to the difference in the light intensity.

Fig. 4. UV–visible spectra of the sample solution after 48 h of irradiation under argon: initial NFPA amount of (A) 3.10, (B) 1.55, and (C) 0.78 mmol (these amounts correspond to concentrations of 135, 67.4, and 33.9 mM, respectively). An aqueous solution ($23\,cm^3$) containing **1** (1.54×10^{-4} mol; 6.70 mM) and NFPA was irradiated with a high-pressure mercury lamp under argon (0.10 MPa). The reaction solutions were transferred into quartz cells (path length: 5 mm) under argon without dilution, and then subjected to measurements. Spectrum D was taken before irradiation (initial amount of NFPA = 1.55 mmol), and the spectrum after 48 h of irradiation under oxygen was identical to D.

[14]. In the present system, the concentration of **1** was sufficient to give highly acidic conditions (pH $\sim$ 0.8); therefore $[PW_{12}O_{40}]^{3-}$ remained as the stable species.

Scheme 1 shows the proposed mechanism for the decomposition of NFPA. Photoexcitation from the ground-state species $[PW_{12}O_{40}]^{3-}$ to the ligand-to-metal charge-transfer excited-state species, $[PW_{12}O_{40}]^{3-*}$ is generally accepted as the initiation process of photocatalysis by **1** (Eq. (1)) [12,13].

$$[PW_{12}O_{40}]^{3-} + h\nu \rightarrow [PW_{12}O_{40}]^{3-*} \tag{1}$$
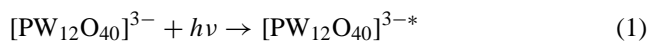
After an electron transfer from NFPA to the excited-state species (Eq. (2)), the resulting reduced complex, $[PW_{12}O_{40}]^{4-}$ is reoxidized to $[PW_{12}O_{40}]^{3-}$ in the presence of oxygen (Eq. (3)).

$$[PW_{12}O_{40}]^{3-*} + NFPA \rightarrow [PW_{12}O_{40}]^{4-} + NFPA^+ \tag{2}$$

$$[PW_{12}O_{40}]^{4-} + O_2 \rightarrow [PW_{12}O_{40}]^{3-} + O_2^- \tag{3}$$

In the absence of oxygen, the reoxidation process is very slow. In fact, when the photoreaction was carried out under argon, conditions under which no catalytic NFPA decomposition occurred, the UV-Vis spectrum after the irradiation showed a broad absorption band in the region from 400 to 1000 nm with absorption maxima at 493 and 752 nm, depending on the initial amount of NFPA (Fig. 4A–C). The new absorption reflects the appearance of the one-electron-reduced complex, $[PW_{12}O_{40}]^{4-}$, which was identified by comparison with its reported spectrum [14,19]. In the spectrum shown in Fig. 4B, where the initial amount of NFPA was 1.55 mmol [(initial NFPA)/(initial **1**) molar ratio = 10/1], the amount of formed $[PW_{12}O_{40}]^{4-}$
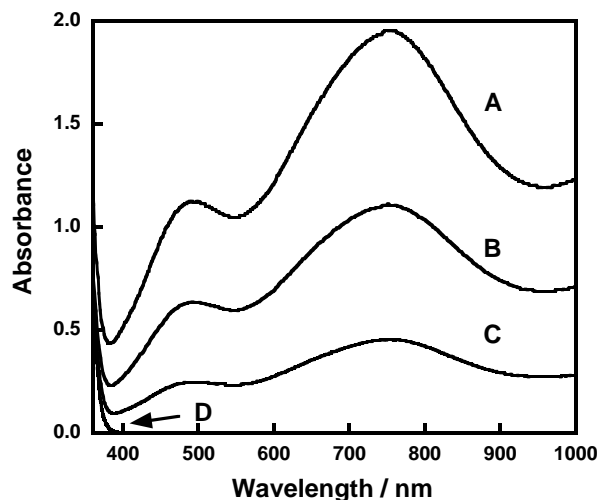
was 2.43×10^{-5} mol; that is, 15.8% of **1** was converted to the reduced complex. The amount of the reduced complex, $[PW_{12}O_{40}]^{4-}$, by irradiation under argon increased as the initial amount of NFPA increased (Table 2).

When the reaction was carried out under argon, the reoxidation of $[PW_{12}O_{40}]^{4-}$ (Eq. (3)) was suppressed, and, therefore, no catalytic reaction occurred. However, a small amount of NFPA decomposition was detected, and that amount increased as the initial amount of NFPA increased (Table 2). In contrast, the small amount of F^- formed under argon was almost constant, which suggests that oxygen is necessary not only for reoxidation of the reduced catalyst but also for F^- formation after NFPA decomposition.

When the reaction was carried out under oxygen, which allowed catalytic decomposition of NFPA, the spectrum after irradiation was the same as that before irradiation (Fig. 4D), and no near-IR absorption was observed. These facts clearly indicate that the catalytic reaction proceeded by a combination of redox reactions between $[PW_{12}O_{40}]^{3-}$ and NFPA, and between $[PW_{12}O_{40}]^{4-}$ and oxygen.

The relaxation of $[PW_{12}O_{40}]^{3-*}$ is fast: for example, the emission lifetime for sodium and trtrapropylammonium salts of $[PW_{12}O_{40}]^{3-}$ is 1.5 ± 0.5 ns [20]. Nevertheless, the excited state is quenched by small quantities (10^{-3} M) of alcohol because of the static mechanism based on the precomplexation of $[PW_{12}O_{40}]^{3-}$ and alcohol [20]. In a similar manner, the enhancement of the catalytic reactivity observed when the initial amount of NFPA was increased (Fig. 3) may indicate that the precomplexation of $[PW_{12}O_{40}]^{3-}$ with NFPA is necessary for the subsequent reaction of
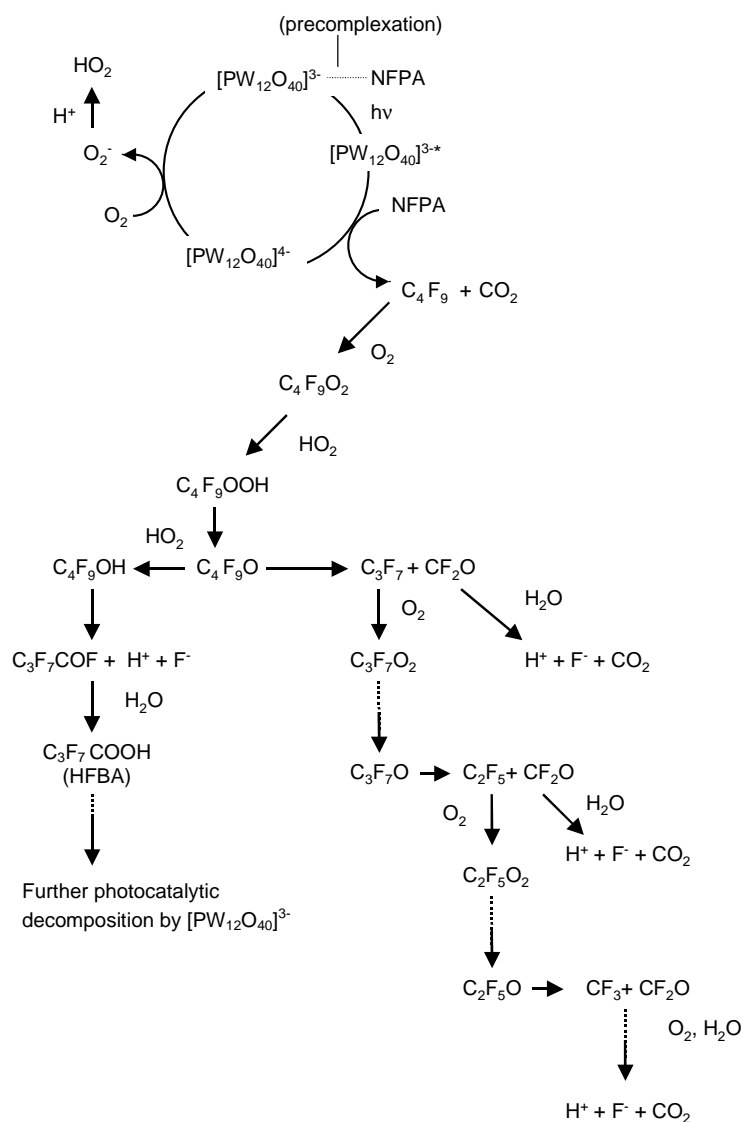
Scheme 1. Proposed mechanism for the decomposition of NFPA.

$[PW_{12}O_{40}]^{3-*}$ with NFPA. The red shift that occurs in the UV-Vis spectrum of **1** in water when the NFPA amount is increased is consistent with precomplexation (Fig. 5). The increase in the formation of the one-electron-reduced complex $[PW_{12}O_{40}]^{4-}$ as the initial amount of NFPA is increased in the reactions under argon (Table 2) may also

reflect the increase in the amount of the excited complex, $[PW_{12}O_{40}]^{3-*}$, that participates in the electron transfer from NFPA, on the basis of the precomplexation between $[PW_{12}O_{40}]^{3-}$ and NFPA. The increase in the amount of $[PW_{12}O_{40}]^{3-*}$ participating in the electron transfer from NFPA leads to an increase in NFPA decomposition, and

Table 2
Products after photoreactions in an argon atmosphere[a]

Entry	Initial NFPA (mmol)	$[PW_{12}O_{40}]^{4-}$ formed[b] (10^{-5} mol)	Yield of $[PW_{12}O_{40}]^{4-\,c}$ (%)	NFPA decomposed (10^{-5} mol)	F^- formed (10^{-5} mol)
1	0.78	1.05	6.8	1.0	4.8
2	1.55	2.43	15.8	1.3	4.9
3	3.10	4.50	29.2	2.9	4.8

[a] Reaction time, 48 h; reaction solution volume, 23 cm^3; initial amount of **1**, 1.54×10^{-4} mol.

[b] Amounts of the one-electron-reduced complex, $[PW_{12}O_{40}]^{4-}$, were calculated using the absorbance at 752 or 493 nm and the reported extinction coefficients at these wavelengths [19].
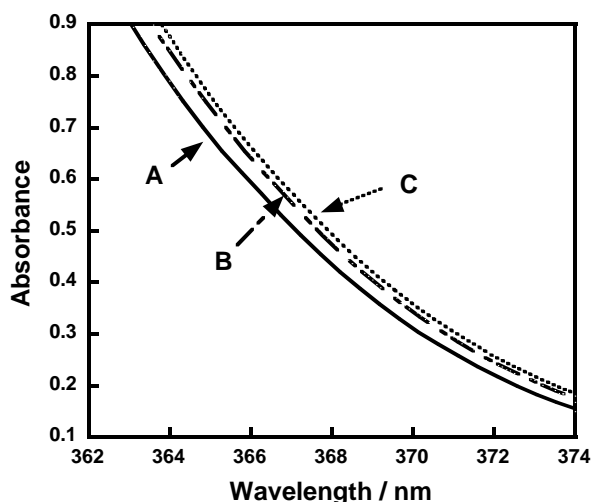
[c] Based on the initial amount of **1**.

Fig. 5. Changes in the UV-Vis spectra of **1** (6.70 mM) in water after the addition of (A) 0, (B) 67.4, and (C) 337 mM NFPA. The path length for the measurements was 1.0 cm.

furthermore, when a large amount of oxygen is present, it leads to an increase in the catalytic formation of F^- and CO_2.

3.2.2. Formation of F^- ions and CO_2 after electron transfer between **1** and NFPA

After electron transfer between the excited complex, $[PW_{12}O_{40}]^{3-*}$, and NFPA (Eq. (2)), the first bond to be cleaved in the one-electron-oxidized NFPA may be the C–C bond between C_4F_9 and COOH. This cleavage produces C_4F_9 radicals and CO_2, probably by the photo-Kolbe mechanism, which has been proposed in the decomposition of acetic acid by a polyoxomolybdate [21] and in the decomposition of TFA by **1** [15]. The C_4F_9 radicals in water should be transformed to $C_4F_9O_2$ in the presence of a large amount of oxygen; CF_3 radicals are transformed to CF_3O_2 in water in an analogous manner [22]. Next, the $C_4F_9O_2$ radicals in water can be decomposed to C_4F_9O [23]; $C_4F_9O_2$ easily abstracts the H from an HO_2 radical to form C_4F_9OOH, and the resulting unstable C_4F_9OOH can decompose to C_4F_9O (Eqs. (4) and (5)).

$$C_4F_9O_2 + HO_2 \rightarrow C_4F_9OOH + O_2 \tag{4}$$

$$C_4F_9OOH \rightarrow C_4F_9O + OH \tag{5}$$

The HO_2 radicals may arise from the O_2^- produced by the reoxidation of the catalyst (Eq. (3)). There is an equilibrium between HO_2 and O_2^- ($pK_a = 4.8$) [24], and because our system is highly acidic (pH $\sim$ 0.8), most of the O_2^- should be transformed into HO_2 (Eq. (6)).

$$O_2^- + H^+ \rightarrow HO_2 \tag{6}$$

Once the C_4F_9O radicals have formed, they can decompose by two pathways. One pathway involves the formation of C_3F_7 and CF_2O (Eq. (7)) [23].

$$C_4F_9O \rightarrow C_3F_7 + CF_2O \tag{7}$$

It has been reported that CF_2O undergoes hydrolysis to give CO_2 and F^- (Eq. (8)) [22].

$$CF_2O + H_2O \rightarrow CO_2 + 2H^+ + 2F^- \tag{8}$$
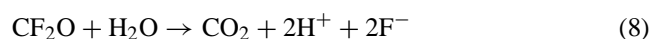
In the presence of a large amount of oxygen, C_3F_7 radicals in water predominantly react with oxygen to form $C_3F_7O_2$, which transforms to C_3F_7O, and then decomposes to C_2F_5 and CF_2O, in an analogous manner that C_4F_9 radicals can transform to C_3F_7 and CF_2O as described above. In a similar manner, the resulting C_2F_5 radicals transform to CF_3 and CF_2O, and CF_3 radicals react with oxygen to form CF_3O_2 [22]. The CF_3O_2 radicals can undergo disproportionation to CF_3OF and CF_2O in water (Eq. (9)) [22].

$$2CF_3O_2 \rightarrow CF_3OF + CF_2O + O_2 \tag{9}$$
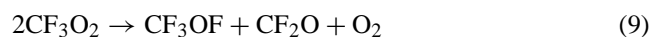
Subsequent hydrolysis of these species results in the formation of CO_2 and F^- [22].

3.2.3. Formation of HFBA during photocatalytic NFPA decomposition

The second decomposition pathway for C_4F_9O radicals involves the formation of HFBA, which was detected during the photocatalytic decomposition of NFPA by **1**. The C_4F_9O radicals (Eq. (5)) react with HO_2 to produce C_4F_9OH (Eq. (10)) [25,26].

$$C_4F_9O + HO_2 \rightarrow C_4F_9OH + O_2 \tag{10}$$
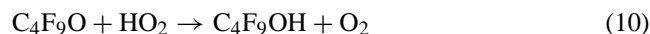
This thermally unstable alcohol forms C_3F_7COF [26], which is hydrolyzed to HFBA (Eqs. (11) and (12)) [27].

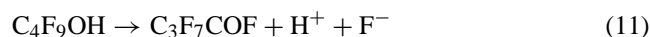$$C_4F_9OH \rightarrow C_3F_7COF + H^+ + F^- \tag{11}$$

Table 3
Photocatalytic decomposition of HFBA, PFPA, and TFA using **1**[a]

Entry	Substrate (initial amount (10^{-4} mol)	Substrate decomposed (10^{-4} mol)	Decomposition yield[b] (%)	F^- formed (10^{-4} mol)	CO_2 formed (10^{-4} mol)	CF_2-unit-shortened species formed (10^{-4} mol)	Turnover number[c]
1	HFBA (15.6)	5.33	34.1	15.5	13.5	PFPA(1.43) TFA (0.49)	3.46
2	PFPA (15.4)	7.14	46.3	17.7	12.7	TFA(3.02)	4.64
3	TFA (15.5)	6.88	44.3	18.3	12.3	–	4.47

[a] Reaction time, 48 h; reaction solution volume, 23 cm³; initial amount of **1**, 1.54×10^{-4} mol; oxygen pressure, 0.55 MPa.

[b] (Mol of decomposed substrate)/(mol of initial amount of substrate) × 100.

[c] (Mol of decomposed substrate)/(mol of initial amount of **1**).

$$C_3F_7COF + H_2O \rightarrow C_3F_7COOH(HFBA) + H^+ + F^- \tag{12}$$
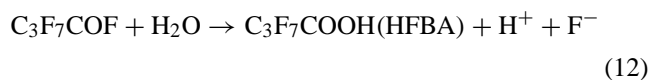
Because the amount of HFBA gradually increased with irradiation time and then decreased (Fig. 2), we examined whether **1** could act as a photocatalyst for the decomposition of HFBA. As expected, HFBA was photocatalytically decomposed, and F^- and CO_2 were formed (Table 3, entry 1). Therefore, the HFBA formed in the decomposition reaction of NFPA can contribute to the formation of F^- and CO_2.

When HFBA was used as the substrate, a small amount of a one-CF_2-unit-shortened species, PFPA, was also detected in addition to F^- ions and CO_2 (Table 3, entry 1), just as HFBA was detected in the photocatalytic decomposition of NFPA by **1**. Furthermore, a two-CF_2-unit-shortened species, TFA, was also detected in the HFBA decomposition. When PFPA was used as the substrate, a small amount of the corresponding one-CF_2-unit-shortened species, TFA, was detected in addition to F^- and CO_2 (Table 3, entry 2). Finally, when TFA was used as the substrate, it produced F^- and CO_2 (Table 3, entry 3). The photocatalytic decomposition of a perfluorinated carboxylic acid to F^- and CO_2 using **1** produces CF_2-unit-shortened species, and these species may act as reaction intermediates.

4. Conclusion

We have shown that tungstic heteropolyacid **1** can photocatalytically cleave the C–F bonds of NFPA in water to produce F^- and CO_2. The reaction proceeds in the presence of oxygen. The maximum turnover for NFPA decomposition reached 8.02 after 48 h of irradiation when the (initial NFPA)/(catalyst **1**) molar ratio was 50/1. The reaction mechanism involves precomplexation between $[PW_{12}O_{40}]^{3-}$ and NFPA and subsequent redox reactions. In the reaction solution, we detected the one-CF_2-unit-shortened species, HFBA, which may also contribute to the formation of F^- and CO_2. Further applications of this method to other perfluorinated acids and the use of polyacid photocatalysts other than **1** are being investigated in our laboratory.

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References

[1] B.D. Key, R.D. Howell, C.S. Criddle, Environ. Sci. Technol. 31 (1997) 2445.
[2] R. Renner, Environ. Sci. Technol. 35 (2001) 154A.
[3] J.P. Giesy, K. Kannan, Environ. Sci. Technol. 36 (2002) 146A.
[4] K.J. Hansen, H.O. Johnson, J.S. Eldridge, J.L. Butenhoff, L.A. Dick, Environ. Sci. Technol. 36 (2002) 1681.
[5] K. Kannan, J.-W. Choi, N. Iseki, K. Senthikumar, D.H. Kim, S. Masunaga, G.P. Giesy, Chemosphere 49 (2002) 225.
[6] K. Kannan, S. Corsolini, J. Falandysz, G. Oehme, S. Focardi, J.P. Giesy, Environ. Sci. Technol. 36 (2002) 3210.
[7] J.P. Giesy, K. Kannan, Environ. Sci. Technol. 35 (2001) 1339.
[8] D.A. Ellis, S.A. Mabury, J.W. Martin, D.C.G. Muir, Nature 412 (2001) 321.
[9] H. Sanderson, T.M. Boudreau, S.A. Mabury, W.-J. Cheong, K.R. Solomon, Environ. Toxicol. Chem. 21 (2002) 1490.
[10] J.-M. Hermann, Catal. Today 53 (1999) 115.
[11] P. Théron, P. Pichat, C. Guillard, C. Pétrier, T. Chopin, Phys. Chem. Chem. Phys. 1 (1999) 4663.
[12] E. Papaconstantinou, Chem. Soc. Rev. 18 (1989) 1.
[13] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113.
[14] H. Einaga, M. Misono, Bull. Chem. Soc. Jpn. 69 (1996) 3435.
[15] H. Hori, Y. Takano, K. Koike, K. Takeuchi, H. Einaga, Environ. Sci. Technol. 37 (2003) 418.
[16] H. Hori, Y. Takano, K. Koike, H. Einaga, T. Ibusuki, Appl. Catal. B: Environ. 46 (2003) 333.
[17] J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskwell, C.A. Johnson (Eds.), Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, IPCC, Cambridge University Press, Cambridge, 2001, p. 389.
[18] J. Pakansky, R. Waltman, J. Phys. Chem. 95 (1991) 1512.
[19] G.M. Varga Jr, E. Papaconstantinou, M.T. Pope, Inorg. Chem. 9 (1970) 662.
[20] M.A. Fox, R. Cardona, E. Gaillard, J. Am. Chem. Soc. 109 (1987) 6347.
[21] T. Yamase, T. Koizumi, J. Chem. Soc. Dalton Trans. (1983) 2205.
[22] S.O. Pehkonen, R.L. Siefert, M.R. Hoffmann, Environ. Sci. Technol. 29 (1995) 1215.
[23] T.J. Wallington, O.J. Nielsen, in: J.R. Barker (Ed.), Progress and problems in atmospheric chemistry, Advance Series of Physical Chemistry, vol. 3, World Scientific, London, 1995, p. 616.
[24] B.H.J. Bielski, D.E. Cabelli, R.L. Arudi, A.B. Ross, J. Phys. Chem. Ref. Data 14 (1985) 1041.
[25] C. Kormann, D.W. Bahnemann, M.R. Hoffmann, Environ. Sci. Technol. 25 (1991) 494.
[26] K. Nohara, M. Toma, S. Kutsuna, K. Takeuchi, T. Ibusuki, Environ. Sci. Technol. 35 (2001) 114.
[27] T.J. Wallington, M.D. Hurley, J.M. Fracheboud, J.J. Orlando, G.S. Tyndall, J. Sehested, T.E. Møgelberg, O.J. Nielsen, J. Phys. Chem. 100 (1996) 18116.